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Atmospheric Measurement Techniques Discussions

Interactive comment on "Development of a photochemical source for the production and calibration of acyl peroxynitrate compounds" *by* P. R. Veres and J. M. Roberts

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The paper describes a novel approach to the calibration of instruments that measure PAN type compounds, such as an I- CIMS spectrometer in this case. The paper is refreshingly concise and I feel compelled to deliver an equally succinct review. The paper is appropriate for AMT. I have three comments that I feel should be addressed before the paper can be published.

1. Figure 2: the authors should explain why the individual chromatograms differ from the mixture chromatogram in absolute and (more importantly) relative peak area and

why the mixture numbers were chosen for the data in table 1 rather than the individual results.

Due to the methods employed, mainly calibration each chromatogram via NOy detection, it was not necessary to achieve identical mixtures for the single component calibration solution and the multicomponent calibration mixture. The mix numbers provided in Table 1 are approximate and therefore the concentrations differ slightly between each single calibration mix and the multicomponent mixtures. The mixture derived sensitivities were included in Table 1 as in the future it will be most efficient to calibrate using the mixture method rather than many single component standards.

2. The authors should comment on the larger relative production of PAN versus the target species when using the chlorides versus the ketones as precursors. Does this not eliminate the acetone contamination from rinsing theory?

We assume the reviewer is pointing out the relatively larger CIMS signal of PAN in the single component standards for methacryloyl chloride and crotonoyl chloride. In the case of these two product species, the sensitivity of the CIMS instrument to MPAN and CPAN is nearly an order of magnitude lower than that for PAN. In reality, the actual amount of MPAN and CPAN produced, as measured by NOy is larger than the amount of PAN produced. Visually this can be seen in the top panel of Figure 2, where the NOy signal for the MPAN peak is approximately 3 times larger than the signal observed on the CIMS at m/z 85. Furthermore the amount of PAN produced using a single component standard is highly variable, lending support for a contaminant rather than an effect of the photochemistry which would be more reproducible (please also see the following response). Further experiments could of course verify either mechanism, however when combined with the use of a GC column it is unnecessary to limit the formation of PAN as it poses no potential for interference on either the CIMS or NOy system.

3. Fix reaction 8

We understand the issue the reviewer is commenting on with respect to reaction 8. After consideration of the reviewer's second comment and going back through the paper, we have come to realize that the explanation given for which equations 6-8 are shown is incorrect. The PAN production observed in the non-ketone synthesis methods generally rules out the production of PAN via the reaction pathway we suggest in equations 6-8 (which is valid for ketone synthesis only). PAN is produced in nearly equivalent mixing ratios using all precursors chlorides and ketones alike. Therefore the most likely method for the production of PAN is via residual acetone in the glass diffusion cells. As such equations 6-8 including relevant discussions have been removed from the manuscript and the changes are reflected in the updated version.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 1457, 2015.